1230050

PATENT SPECIFICATION (11) 1230050

NO DRAWINGS

(21) Application No. 45529/70 (22) Filed 5 April 1968

(61) Patent of Addition to No. 1 224 082 dated 25 March 1969

(62) Divided out of No. 1 224 082

(23) Complete Specification filed 25 March 1969

(45) Complete Specification published 28 April 1971

(51) International Classification A 01 n 9/22

(52) Index at acceptance A5E 1C17 1C4B2 1C4B3 1C4B4

(72) Inventor KARL AYAD

(54) USE OF NITROAMINOPYRIDINES AS HERBICIDES

ERRATUM

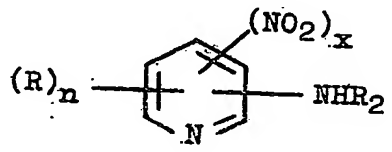
SPECIFICATION NO. 1,230,050

Page 1, Heading, *for* '(61) Patent of Addition to No. 1,224,082 dated 25 March 1969' *read* '(61) Patent of Addition to No. 1,219,633 dated 13 January 1969 as improved upon or modified by No. 1,224,082 dated 25 March 1969'

THE PATENT OFFICE
4 November 1971

R 6357/4

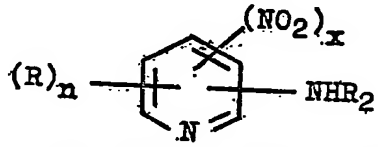
the formula:



where R is alkyl of from 1 to 4 carbon atoms; x is 2 and n is 1 or 2 when R_2 is alkanoyl of up to 6 carbon atoms, or x and n are each 1 or 2 and the sum of x and n is 3 when R_2 is hydrogen; the NO_2 group or groups occupy one or both of positions 3 and 5; the NHR_2 group occupies a 2, 4 or 6 position and the R group or groups occupy one or two of the 2, 4 and 6 positions remaining, and the use of these compounds in inhibiting the growth of vegetation. We have now found that closely related nitroaminopyridines also have this use.

The invention comprises a method of inhibiting the growth of vegetation which comprises applying to soil infested with plant seeds or to plant surfaces, a herbicidal concentration of a nitroaminopyridine base having the formula:

or 5 carbon atoms in the ring; each R is a halogen atom or a substituted or unsubstituted hydrocarbyl radical, or a $-SO_3H$, $-CN$, $-OR_3$, $-SR_3$ or $-COOR_3$ group where R_3 represents hydrogen or a substituted or unsubstituted hydrocarbyl radical, and where the group $-NO_2$ occupies one or both the positions 3 and 5 and the $-NR_1R_2$ group occupies one or two of the positions 2, 4 and 6; with the proviso that, where the compound is a base or an acid addition salt, x, y and n each have the value 1, and the groups $-NR_1R_2$, $-NO_2$ and R occupy the 2, 3 and 5 positions respectively, then either (a) R is a radical selected only from alkenyl and alkynyl groups having 1 to 4 carbon atoms or substituted or unsubstituted hydrocarbyl groups having 5 or more carbon atoms, or $-SO_3H$, $-CN$, $-OR_3$, $-SR_3$, $-CF_3$ or $-COOR_3$ groups or (b) at least one of R_1 and R_2 is an acyl group; other than a nitroaminopyridine base having the formula



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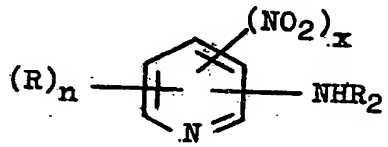
(72) Inventor KARL AYAD

(54) USE OF NITROAMINOPYRIDINES AS HERBICIDES

(71) We, MONSANTO CHEMICALS LIMITED, a British Company of, Monsanto House, 10—18 Victoria Street, London, S.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

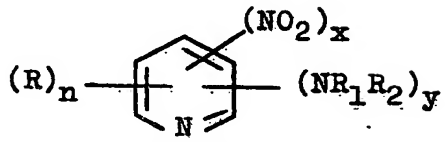
This invention relates to a method of inhibiting the growth of vegetation using nitroaminopyridines having herbicidal activity.

In our pending British Patent Specification No. 16436/68 (Serial No. 1224082) we describe and claim nitroaminopyridines having the formula:

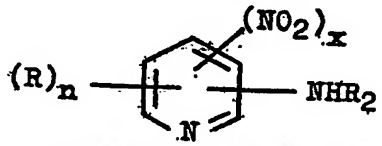


where R is alkyl of from 1 to 4 carbon atoms; x is 2 and n is 1 or 2 when R_2 is alkanoyl of up to 6 carbon atoms, or x and n are each 1 or 2 and the sum of x and n is 3 when R_2 is hydrogen; the NO_2 group or groups occupy one or both of positions 3 and 5; the NHR_2 group occupies a 2, 4 or 6 position and the R group or groups occupy one or two of the 2, 4 and 6 positions remaining, and the use of these compounds in inhibiting the growth of vegetation. We have now found that closely related nitroaminopyridines also have this use.

The invention comprises a method of inhibiting the growth of vegetation which comprises applying to soil infested with plant seeds or to plant surfaces, a herbicidal concentration of a nitroaminopyridine base having the formula:



or an N-oxide or salt of such a nitroaminopyridine base, where x and y are each 1 or 2; n is 0, 1 or 2 provided that the sum of x, y and n does not exceed 5; R_1 and R_2 are the same or different and represent hydrogen, substituted or unsubstituted hydrocarbyl or acyl radicals, or together with the nitrogen atom represent a single heterocyclic ring having 4 or 5 carbon atoms in the ring; each R is a halogen atom or a substituted or unsubstituted hydrocarbyl radical, or a $—SO_3H$, —CN, $—OR_3$, $—SR_3$, or $—COOR_3$ group where R_3 represents hydrogen or a substituted or unsubstituted hydrocarbyl radical, and where the group $—NO_2$ occupies one or both the positions 3 and 5 and the $—NR_1R_2$ group occupies one or two of the positions 2, 4 and 6; with the proviso that, where the compound is a base or an acid addition salt, x, y and n each have the value 1, and the groups $—NR_1R_2$, $—NO_2$ and R occupy the 2, 3 and 5 positions respectively, then either (a) R is a radical selected only from alkenyl and alkynyl groups having 1 to 4 carbon atoms or substituted or unsubstituted hydrocarbyl groups having 5 or more carbon atoms, or $—SO_3H$, —CN, $—OR_3$, $—SR_3$, $—CF_3$ or $—COOR_3$ groups or (b) at least one of R_1 and R_2 is an acyl group; other than a nitroaminopyridine base having the formula



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where R is alkyl of from 1 to 4 carbon atoms; x is 2 and n is 1 or 2 when R_2 is alkanoyl of up to 6 carbon atoms, or x and n are each 1 or 2 and the sum of x and n is 3 when R_2 is hydrogen; the NO_2 group or groups occupy one or both of positions 3 and 5; the NHR_2 group occupies a 2, 4 or 6 position and the R group or groups occupy one or two of the 2, 4 and 6 positions remaining.

The invention also includes a herbicidal composition comprising a nitroaminopyridine base as defined above or an oxide or salt of such a base, in admixture with a diluent or carrier and a surface active agent.

Classes of nitroaminopyridine bases and salts of such nitroaminopyridine bases which are of special use in the method of inhibiting the growth of vegetation of the invention and in the herbicidal compositions of the invention are those for which R_1 is hydrogen, R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms and R or each R is chlorine, bromine or alkyl of up to 4 carbon atoms and

(a) x is 1 or 2, y is 1 and n is 2,
(b) x is 2, y is 1 and n is 1, or
(c) x is 1, y is 1, n is 1 and the NR_1R_2

and NO_2 groups respectively occupy either the 2 and the 5 positions or the 4 and the 3 positions in the pyridine nucleus.

The term hydrocarbyl as used above is taken to include alkyl, alkenyl, alkynyl, cycloalkyl and aryl radicals. More specifically the preferred non-aromatic hydrocarbyl radicals are those having from 1 to 6 carbon atoms such as methyl-, ethyl-, isopropyl-, t-butyl-, hexyl-, cyclohexyl-, propenyl, and n-butynyl-radicals and the preferred aromatic hydrocarbyl radicals are those having from 6 to 12 carbon atoms such as phenyl-, tolyl-, benzyl-, xylyl-, and naphthyl- radicals.

The herbicidal compounds useful in the invention falling in the category of special interest are those in which R or each R is an alkyl or haloalkyl group having 1 to 4 carbon atoms such as for example methyl, ethyl, isopropyl, trichloromethyl and trifluoromethyl, a halogen atom such as for example bromine, chlorine or fluorine, or an $-SO_3H$, $-CN$, $-SH$ or $COOR_3$ group, where R_3 is hydrogen or an alkyl group having 1 to 4 carbon atoms, and in particular those in which R or each R is methyl, chlorine or bromine.

Examples of substituted hydrocarbyl groups from which R_1 and R_2 may be selected include cyano, halo, hydroxy, alkoxy and poly-(oxyalkylene)oxy - substituted hydrocarbyl groups. Acyl groups may be selected from alkanoyl groups, particularly those containing up to 6 carbon atoms, and sulphonyl groups, for example methane sulphonyl and benzene sulphonyl. Preferred compounds useful in the invention are those in which R_1 is hydrogen and R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms.

Examples of the herbicidal nitroaminopyridines useful in the invention include 3 - nitro - 4 - aminopyridine; 5 - nitro - 3 - chloro - 2 - aminopyridine; 5 - nitro - 6 - methyl - 2 - aminopyridine; 3,5 - di - nitro - 2 - aminopyridine; 5 - trifluoromethyl - 3 - nitro - 2 - aminopyridine; 3 - nitro - 2 - aminopyridine-5-carboxylic acid; 6 - methyl - 3 - nitro - 2 - aminopyridine; 6 - chloro - 3 - nitro - 2 - aminopyridine; 4 - methyl - 3 - nitro - 2 - aminopyridine; 3,5 dinitro - 4 - aminopyridine; 3 - nitro - 6 - methyl - 4 - aminopyridine; 6 - chloro - 3 - nitro - 4 - aminopyridine; 2 - chloro - 3 - nitro - 4 - aminopyridine; 5 - nitro - 3 - methyl - 2 - methylaminopyridine; 5 - chloro - 3 - nitro - 2 - acetamidopyridine; 5 - nitro - 6 - methyl - 2 - acetamidopyridine; 5 - nitro - 3 - trichloromethyl - 2 - aminopyridine; 6 - trifluoromethyl - 3 - nitro - 4 - aminopyridine; 3 - nitro - 4 - chloro - 2 - aminopyridine; 2,6 - dichloro - 3 - nitro - 4 - aminopyridine; the N - oxides and salts of the above compounds.

The salts of the pyridine bases include the addition salts with inorganic acids, for example the hydrohalides such as for instance the hydrochlorides and hydrobromides, the sulphates and the sulphamates, and those with organic acids, for example the oxalates, chloroacetates and benzenesulphonates. Also included are the quarternary ammonium salts, for instance the alkyl and aralkyl pyridinium halides and sulphates. The alkyl group attached to the nitrogen atom of the pyridine ring in an alkyl pyridinium salt can for example be one having up to 20 carbon atoms, and the aralkyl group in an aralkyl pyridinium salt can for example be a benzyl or substituted benzyl group.

The herbicidal nitroaminopyridines useful in the invention are conveniently made by the action of fuming nitric acid on the corresponding aminopyridine in the presence of concentrated sulphuric acid. The reaction may initially result in the formation of a nitraminopyridine and where, under the conditions of the reaction, this is stable, the temperature of the reaction mixture is raised to bring about the rearrangement of the nitraminopyridine to a corresponding nitroaminopyridine. The reaction may however proceed directly to the nitroaminopyridine if conducted at higher temperatures.

The herbicidal composition of the invention can be liquid or solid, and a liquid composition can be a solution, suspension or emulsion. The surface active agent is present to stabilise the composition, to facilitate its application, and/or to improve biological activity.

A composition can contain a nitroaminopyridine derivative as the only active ingredient, or one or more other compounds having

similar properties can be present. Thus the nitroaminopyridine derivatives may be used in combination with known herbicides in order to provide enhanced biological effectiveness. The use of various herbicides in combination at the time of a single application or sequentially is common in practice. Herbicides which may be used in combination with the compounds of this invention include but are not limited to: substituted phenoxyaliphatic acids such as 2,4 - dichlorophenoxyacetic acid; 2,4,5 - trichlorophenoxyacetic acid, 2-methyl-4 - chlorophenoxyacetic acid and the salts, esters and amides thereof; triazine derivatives such as 2 - chloro-4-ethylamino-6-isopropylamino - *s* - triazine; 2,4 - bis - (isopropylamino) - 6 - methoxy - *s* - triazine and 2 - methylmercapto - 4,6 - bis - (isopropylamino) - *s* - triazine; urea derivatives such as 3 - (3,4-dichlorophenyl) - 1,1 - dimethylurea and 3 - (*m* - trifluoromethylphenyl)-1,1-dimethylurea and 3 - (3,4 - dichlorophenyl)-1 - methoxy - 1 - methylurea; pyridylium derivatives such as 1:1′ - ethylene - 2,2′ - dipyridylium dihalides; acetanilides such as N - isopropyl - α - chloro - acetanilide, and 2 - chloro - 2′,6′ - diethyl - N - methoxymethyl acetanilide; acetamides such as N,N - diallyl-α-chloroacetamide; carbamates such as ethyl - N,N - di - *n* - propylthiocarbamate, and 2,3 - dichloroallyl diisopropyl - thiolcarbamate; substituted uracils such as 5 - bromo - 3 - *sec* - butyl - 6 - methyluracil; substituted anilines such as N,N - dipropyl-α,α,α - trifluoro - 2,6 - dinitro - *p* - toluidine; and pyridazone derivatives such as 5 - amino - 4 - chloro - 2 - phenyl - 3 - (2H) - pyridazinone.

A solution of a nitroaminopyridine derivative is one in an organic solvent, for example an alcohol; a ketone; a hydrocarbon, for instance white spirit, solvent naphtha or kerosene; or a halogenated hydrocarbon, for instance perchloroethylene. The surface active agent is selected according to its solubility in the solvent, and non-ionic surface active agents, for example ethers or esters of polyethylene glycols, are generally suitable.

Compositions that are suspensions can be simple ones of the nitroaminopyridine derivative in an aqueous medium with the surface active agent functioning as a stabiliser. The surface active agent can be, for instance, a non-ionic agent as exemplified above, or an ionic surface active agent, for example a soap or a synthetic material such as the sodium salt of a long-chain alkylated aromatic sulphonic acid.

A herbicidal emulsion of the invention is usually an aqueous emulsion, and can be obtained by emulsifying a solution of a nitroaminopyridine derivative in a suitable organic solvent, generally one that is water-immiscible, with water in the presence of a surface active agent. The surface active agent can be ionic or non-ionic in character.

Compositions which are solids can for instance be those in which the carrier in an inert powder such as for instance kieselguhr or talc. The presence of the surface active agent in such a composition facilitates its application and/or improves its biological activity.

The proportion of the herbicide employed in the composition will of course vary according to the nature of the composition and the proposed application. Compositions intended for direct application can contain, for example, from 0.001 to 2% by weight of nitroaminopyridine and usually contain an amount within the range 0.01 to 1% by weight. Compositions that are concentrates and are intended to be diluted before use may contain for instance from 5 to 95% by weight of nitroaminopyridine, for example 10%, 25%, 50% or 80% of nitroaminopyridine.

The dosage at which a nitroaminopyridine derivative of the invention or a herbicidal composition containing such a nitroaminopyridine derivative should be applied to obtain the optimum effect, will of course depend on the particular crop concerned and the particular weeds that are to be controlled. Also the activity or selectivity of a herbicide can be modified accordling to whether it is applied to a "pre-emergent" or "post-emergent" stage of plant growth. Normally however, in foliar treatment for the modification of vegetative growth, the nitroaminopyridines are applied in amounts from about 1 to about 50 or more pounds per acre. In applications to soil for the modification of the growth of germinant seeds, germinative seeds, emerging seedlings and established vegetation, the nitroaminopyridines are applied in amounts from about 0.1 to about 25 or more pounds per acre. In such soil applications, it is desirable that the nitroaminopyridines be distributed to a depth of at least 0.2 inches. In selective pre-emergence phytotoxic applications the nitroaminopyridines are usually applied in amounts from about 0.1 to 5 pounds per acre. It is believed that one skilled in the art can readily determine from the teachings of this specification, including examples, the general procedure for any application.

The invention is illustrated by the following Examples.

Example 1

This Example sets out the results of screening tests on the herbicidal activities of various herbicidal nitroaminopyridines.

The pre-emergence herbicidal ratings of several compounds of the invention were determined in a greenhouse test in which a specific number of seeds of a number of different plants, each representing a principal

botanical type, were planted in greenhouse flats.

A good grade of top soil was placed in aluminium pans and compacted to a depth of ¾ to ½ inch from the top of the pan. On top of the soil were placed a pre-determined number of seeds of various plant species. The seeds were covered with soil which was struck level with the top of the pan, then a known amount of the chemical was applied to the exposed surface. After treatment the pans were moved into a greenhouse bench where they were watered from below as needed to give adequate moisture for germination and growth.

Approximately 14 days after seeding and treating, the plants were observed and the results recorded. The herbicidal rating was obtained by means of a fixed scale based on the average per cent germinaiton of each seed lot.

The contact herbicidal activities of the same compounds were determined in greenhouse tests. The nitroaminopyridine derivative to be tested was applied in spray form to plants of a given age of the same grasses and broadleaf plants as used in the above pre-emergence tests, grown from seed in aluminium pans. After the plants were the desired age, each aluminium pan was sprayed with a given volume of a 0.5% concentration solution of the test chemical, corresponding to a rate of approximately 10 pounds per acre. This herbicidal solution was prepared from an aliquot of a 2% solution of the test compound in acetone, a known amount of a cyclohexanone-emulsifying agent mix, and sufficient water to make up to volume. The emulsifying agent was a mixture comprising 35 weight % of butylamine dodecylbenzene sulphonate and a 65 weight % of a tall oil-ethylene oxide condensate having about 6 moles of ethylene oxide per mole of tall oil. The injuries to the plants were then observed approximately 14 days later and are reported in the Table I. The herbicidal ratings are defined as follows:

Pre-emergent tests	*Post-emergent tests*
0 No phytotoxicity	0 No phytotoxicity
1 Slight phytotoxicity	1 Slight phytotoxicity
2 Moderate phytotoxicity	2 Moderate phytotoxicity
3 Severe phytotoxicity	3 Severe phytotoxicity
	4 Death

a rating of 3 on either scale is considered very good.

The compounds tested were:

3,5-dinitro-4-aminopyridine — A
4-methyl-3-nitro-2-aminopyridine — B
6-methyl-5-nitro-2-aminopyridine — C
3-nitro-4-aminopyridine — D

TABLE 1

Seed Type	Post-emergence or Contact Test 0.5% Concentration				Pre-emergence Test 10 lbs. per acre.		
	A	B	C	D	A	B	C
Morning Glory	2	2	2	2	0	0	3
Wild Oat	1	0	0	1	1	0	3
Brome	2	1	0	1	1	1	1
Rye Grass	1	0	0	0	1	2	3
Radish	3	1	3	4	1	1	3
Sugar Beet	4	0	3	1	2	1	3
Foxtail	2	2	0	2	3	2	3
Crab Grass	2	2	0	3	3	2	3
Pigweed	3	3	3	4	3	2	3
Soybean	0	1	2	1	0	0	2
Wild Buckwheat	4	2	4	0	1	3	3
Tomato	4	3	3	2	1	0	3
Sorghum	0	2	0	2	1	0	1

EXAMPLE 2

This Example gives the results of the evaluation of further nitroaminopyridines by the methods described in Example 1.

The compounds were:

3,5-Dinitro-2-aminopyridine	E
2-Chloro-5-nitro-4-aminopyridine	F
2-Chloro-3-nitro-4-aminopyridine	G
2,6-Dichloro-3-nitro-4-aminopyridine	H
5-Nitro-6-methyl-2-acetamidopyridine	I

Seed Type	Contact 0.5% Concentration					Pre-emergence 10 lbs. per acre				
	>E	F	G	H	I	E	F	G	H	I
Morming Glory	0	3	1	2	2	3	0	0	0	3
Wild Oat	1	1	0	0	0	0	0	0	0	3
Brome	2	1	1	2	0	0	0	0	0	3
Rye Grass	1	1	0	2	0	0	0	0	1	3
Radish	0	3	2	4	2	3	0	2	1	3
Sugar Beet	1	2	1	3	2	3	0	1	2	3
Foxtail	3	3	1	2	0	1	2	0	0	3
Crab Grass	3	3	2	2	1	1	3	3	3	3
Pigweed	3	4	3	3	4	3	2	3	3	3
Soybean	0	1	1	2	1	1	0	0	0	3
Wild Buckwheat	0	2	1	4	3	3	0	3	1	3
Tomato	0	–	–	4	2	3	3	3	0	3
Sorghum	3	2	1	0	0	0	0	0	0	2

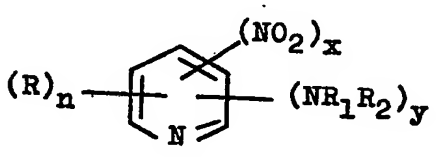
Compounds F and H were further evaluated as contact herbicides at 0.2% concentration against the following range of plants and with the following results:

	F	H
Cotton	1	0
Corn	1	1
Soybean	1	1
Cocklebur	1	2
Crab Grass	3	4
Lambs quarter	4	4
Wild Oat	0	2
Smartweed	4	4
Brome	1	3
Pigweed	3	4
Barnyard Grass	2	3
Sugar beet	1	2
Wheat	0	1
Velvet leaf	2	2
Rice	1	1
Coffee weed	2	2

These figures show a useful degree of selective herbicidal activity.

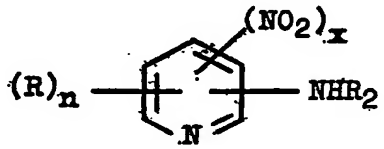
WHAT WE CLAIM IS:—

1. A method of inhibiting the growth of vegetation which comprises applying to soil infested with plant seeds or to plant surfaces, a herbicidal concentration of a nitroaminopyridine base having the formula:



or an N-oxide or salt of such a nitroaminopyridine base, where x and y are each 1 or 2; n is 0, 1 or 2 provided that the sum of x, y and n does not exceed 5; R_1 and R_2 are the same or different and represent hydrogen, substituted or unsubstituted hydrocarbyl or acyl radicals, or together with the nitrogen atom represent a single heterocyclic ring having 4 or 5 carbon atoms in the ring; each R is a halogen atom or a substituted or unsubstituted hydrocarbyl radical, or a $-SO_3H$, $-CN$, $-OR_3$, $-SR_3$ or $-COOR_3$ group where R_3 represents hydrogen or a substituted or unsubstituted hydrocarbyl radical, and where the group $-NO_2$ occupies one or both the positions 3 and 5 and the $-NR_1R_2$ group occupies one or two of the positions 2, 4 and 6; with the proviso that, where the compound is a base or an acid addition salt, x, y and n each have the value 1, and the groups $-NR_1R_2$, $-NO_2$ and R occupy the 2, 3 and 5 positions respectively, then either (a) R is a radical selected only from alkenyl and alkynyl groups having 1 to 4 carbon atoms or substituted or unsubstituted hydrocarbyl groups having 5 or more carbon atoms, or $-SO_3H$, $-CN$, $-OR_3$, $-SR_3$, $-CF_3$ or

—$COOR_3$ groups or (b) at least one of R_1 and R_2 is an acyl group; other than a nitroaminopyridine base having the formula



where R is alkyl of from 1 to 4 carbon atoms; x is 2 and n is 1 or 2 when R_2 is alkanoyl of up to 6 carbon atoms, or x and n are each 1 or 2 and the sum of x and n is 3 when R_2 is hydrogen; the NO_2 group or groups occupy one or both of positions 3 and 5; the NHR_2 group occupies a 2, 4 or 6 position and the R group or groups occupy one or two of the 2, 4 and 6 positions remaining.

2. A method according to Claim 1, in which there is employed a nitroaminopyridine base or a salt of a nitroaminopyridine base, where, in the formula in Claim 1, x has the value 1 or 2, y is 1, n is 2, R_1 is hydrogen, R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms, and each R is chlorine, bromine, or alkyl of up to 4 carbon atoms.

3. A method according to Claim 2, which comprises applying a herbicidal concentration of 2,6 - dichloro - 3 - nitro - 4 - aminopyridine.

4. A method according to Claim 1, in which there is employed a nitroaminopyridine base or a salt of a nitroaminopyridine base, where, in the formula in Claim 1, x is 2, y is 1, n is 1, R_1 is hydrogen, R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms, and R is chlorine, bromine, or alkyl of up to 4 carbon atoms.

5. A method according to Claim 1, which comprises applying a herbicidal concentration of 3,5 - dinitro - 2 - aminopyridine.

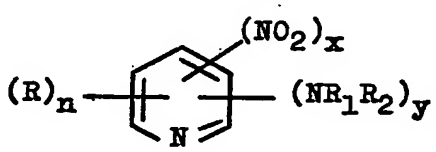
6. A method according to Claim 1, which comprises applying a herbicidal concentration of 3,5-dinitro-4-aminopyridine.

7. A method according to Claim 1, in which there is employed a nitroaminopyridine base or a salt of a nitroaminopyridine base, where, in the formula in Claim 1, x is 1, y is 1, n is 1, R_1 is hydrogen, R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms, R is chlorine, bromine or alkyl of up to 4 carbon atoms, and wherein the NR_1R_2 and NO_2 groups respectively occupy either the 2 and the 5 positions or the 4 and the 3 positions in the pyridine nucleus.

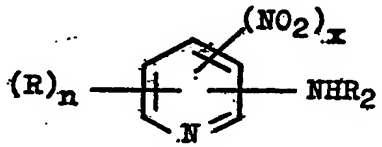
8. A method according to Claim 7, which comprises applying a herbicidal concentration of 6 - methyl - 5 - nitro - 2 - aminopyridine, 6 - chloro - 3 - nitro - 4 - aminopyridine, or 2 - chloro - 3 - nitro - 4 - aminopyridine.

9. A method according to Claim 7, which comprises applying a herbicidal concentration of 6-methyl-5-nitro-2-acetylaminopyridine.

10. A herbicidal composition containing a nitroaminopyridine base having the formula:



or an N-oxide or salt of such a nitroaminopyridine base, where x and y are each 1 or 2, n is 0, 1 or 2 provided that the sum of x, y and n does not exceed 5; R_1 and R_2 are the same or different and represent hydrogen, substituted or unsubstituted hydrocarbyl or acyl radicals, or together with the nitrogen atom represent a single heterocyclic ring having 4 or 5 carbon atoms in the ring; R is a halogen atom or a substituted or unsubstituted hydrocarbyl radical, or a $—SO_3H$, —CN, $—OR_3$, $—SR_3$, or $—COOR_3$ group where R_3 represents hydrogen or a substituted or unsubstituted hydrocarbyl radical, and where the group $—NO_2$ occupies one or both the positions 3 and 5 and the $—NR_1R_2$ group occupies one or two of the positions 2, 4 and 6; with the proviso that, where the compound is a base or an acid addition salt, x, y and n each have the value 1, and the groups $—NR_1R_2$, $—NO_2$ and R occupy the 2, 3 and 5 positions respectively, then either (a) R is a radical selected only from alkenyl and alkynyl groups having 1 to 4 carbon atoms or substituted or unsubstituted hydrocarbyl groups having 5 or more carbon atoms, or $—SO_3H$, —CN, $—OR_3$, $—SR_3$, $—CF_3$ or $—COOR_3$ groups, or (b) at least one of R_1 and R_2 is an acyl group; other than a nitroaminopyridine base having the formula:



where R is alkyl of from 1 to 4 carbon atoms; x is 2 and n is 1 or 2 when R_2 is alkanoyl of up to 6 carbon atoms, and x and n are each 1 or 2 and the sum of x and n is 3 when R_2 is hydrogen; the NO_2 group or groups occupy one or both of positions 3 and 5; the NHR_2 group occupies a 2, 4 or 6 position and the R group or groups occupy one or two of the 2, 4 and 6 positions remaining; in admixture with a diluent or carrier and a surface active agent.

11. A herbicidal composition according to Claim 10 containing a nitraminopyridine base or a nitroaminopyridine salt where in the formula of the nitroaminopyridine x has the value 1 or 2, y is 1, n is 2, R_1 is hydrogen, R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms, each R is chlorine, bromine, or alkyl of up to 4 carbon atoms.

12. A herbicidal composition according to Claim 11 containing 2,6-dichloro-3-nitro-4-aminopyridine.

13. A herbicidal composition according to Claim 10 containing a nitroaminopyridine base or a salt of a nitroaminopyridine base, where, in the formula of the nitroaminopyridine, x is 2, y is 1, n is 1, R_1 is hydrogen, R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms, R is chlorine, bromine, or alkyl of up to 4 carbon atoms.

14. A herbicidal composition according to Claim 10 containing 3,5-dinitro-2-aminopyridine.

15. A herbicidal composition according to Claim 10 containing 3,5 - dinitro - 4 - aminopyridine.

16. A herbicidal composition according to Claim 10 containing a nitroaminopyridine base or a salt of a nitro aminopyridine base, where, in the formula of the nitroaminopyridine x is 1, y is 1, n is 1, R_1 is hydrogen, R_2 is hydrogen or an alkanoyl group containing up to 6 carbon atoms, R is chlorine, bromine or aralkyl of up to 4 carbon atoms, and wherein the NR_1R_2 and NO_2 groups respectively occupy either the 2 and the 5 positions or the 4 and the 3 positions in the pyridine nucleus.

17. A herbicidal composition according to Claim 16 containing 6 - methyl - 5 - nitro - 2 - aminopyridine, 6 - chloro - 3 - nitro - 4 - aminopyridine, or 2 - chloro - 3 - nitro - 4 - aminopyridine.

18. A herbicidal composition according to Claim 16 containing 6 - methyl - 5 - nitro - 2 - acetylaminopyridine.

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